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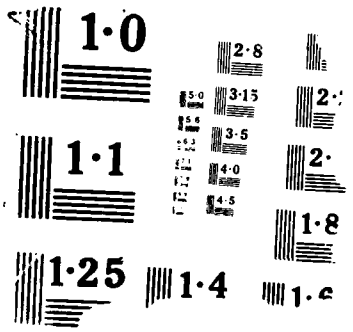
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Picosecond Transient Reflectivity of Unpinned Gallium Arsenide (100) Surfaces

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This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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Surface recombination was measured for photowashed and unwashed GaAs using picosecond transient photoreflectance methods. The results for the washed surfaces clearly demonstrate slow surface recombination that is accurately described by an ambipolar diffusion model. The fast decay observed for unwashed samples implies rapid surface recombination involving a more complex mechanism.

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PREFACE

The authors wish to acknowledge extremely helpful technical discussions with Dr. Steven Moss concerning recombination processes and transient probe experiments.

CONTENTS

FIGURES

I. INTRODUCTION

Until quite recently, nearly all investigations supported the existence of pinned surfaces on gallium arsenide crystals. This major technological problem was attributed to surface states of various possible origin. In one widely accepted model, proposed by Spicer et al.,[1] the surface states derive from inherent defect vacancy sites. Other models, such as that of Woodall and co-workers at IBM,[2] attributed pinning to surface impurity states, consisting of arsenic metal or arsenic oxide films with mid-bandgap states. Regardless of model, the practical effect is to make it difficult to change interface potential. This provides a formidable problem in development of high efficiency GaAs field effect devices.

Recently the IBM group[3] performed interesting and suggestive experiments on (100) GaAs that produced unpinned surfaces. Their procedure involved washing the surface with ultrapure water in the presence of above-bandgap laser irradiation. Unpinned behavior was observed immediately after washing. Photoluminescence yields measured from regions near the surface increased dramatically. The yields declined slowly with time, subsequent to exposure to ambient atmospheric conditions. Metal insulator semiconductor capacitors were constructed from the washed material. They displayed classical unpinned capacitance-voltage characteristics.

In this report we present picosecond transient photoreflectance studies of (100) GaAs that are largely consistent with the recent IBM results and model. We measured changes in reflectivity of a probe beam induced by an above-bandgap pump pulse. Time delays for the probe beam were scanned over the range 0 to 0.5 ns. Results obtained before and after photochemical washing were compared for a variety of samples. As described below, the unwashed samples displayed complex kinetic behavior that varied appreciably from sample to sample and even for different sides of the same sample. However, the photochemically washed samples yielded uniform results that provide textbook examples of diffusion controlled recombination processes. We demonstrate that surface recombination velocities are exceedingly small on photochemically

cleaned (100) surfaces of doped and undoped GaAs and that a simple model accurately describes recombination. Furthermore, we show that surface recombination processes dominate transient reflectivity results for uncleaned, pinned GaAs samples.

II. EXPERIMENTAL

A variety of commercial GaAs samples, including intrinsic, chromium doped, and silicon n-doped materials, was studied. The doped samples had typical dopant concentrations of 1×10^{17} cm^{-3}. Unwashed sample surfaces were nominally clean; however, no cleaning procedure was used.

Experiments were performed with a synchronously pumped, mode-locked dye laser system. The pump source was an argon ion laser operated at a pulse repetition rate of 228 MHz at 514.5 nm. This laser pumped two dye lasers operated with styryl 9 dye. Most experiments were performed with the pump laser tuned to 812 nm, substantially above the room temperature bandgap of GaAs, and the probe laser was operated in the region of 840 nm, still somewhat above bandgap at room temperature. The pump beam was amplitude modulated at 14 MHz, and both pump and probe were combined in a copropagating configuration. They were focused to approximately 10 μm diameter at the GaAs surface. A typical cross-correlation pulsewidth measurement yielded a width of 12 ps, and the cw pump beam power was approximately 30 mW. Based on the absorption coefficient of 1×10^{4} cm^{-1}, the peak injected carrier density, assuming loss processes are slower than the pulsewidth, would be about 1×10^{18} cm^{-3}. In this regime of injected carrier density, contributions from nonlinear recombination processes and density dependent diffusion should be negligible. The reflected probe beam was separated from the pump by a monochromator, and a lock-in amplifier was used to measure the signal modulated at the 14 MHz modulation frequency of the pump laser.

III. RESULTS

Typical transient reflectivity measurements for a washed and unwashed GaAs surface are shown in Fig. 1. The unwashed results (plotted on a semi-logarithmic scale) are biexponential with a fast and a slow component. The fast component decays with characteristic 1/e times ranging from 30-70 ps, and the slow component decays in times greater than 200 ps. The relative amplitudes of the two processes, and even the sign of the reflectivity changes, depend on samples and on probe wavelengths. Detailed results for the range of samples studied are too varied and complex to be treated in this report. However, they are described generally by the above characteristics. Measurements were entirely reproducible for each individual sample and did not vary appreciably across an individual sample face. However, there were major differences between opposite sides of (100) wafers.

Results from the washed surfaces were remarkably uniform. The reflectivity change increased appreciably in amplitude, relative to the unwashed samples, and the decay was generally slower. A typical example, displaying the nonexponential decay, is shown in Fig. 1. It is characterized by fast decay over the first 50 ps and slower decay at times longer than 200 ps. These measurements were recorded within an hour of washing. Only small changes were observed up to a day after washing, with storage under ambient conditions. Similar results were observed for all washed n-type, intrinsic, and chromium doped samples. (The IBM group observed substantially more rapid deterioration of washed sample behavior for samples exposed to ambient conditions than we observed.)

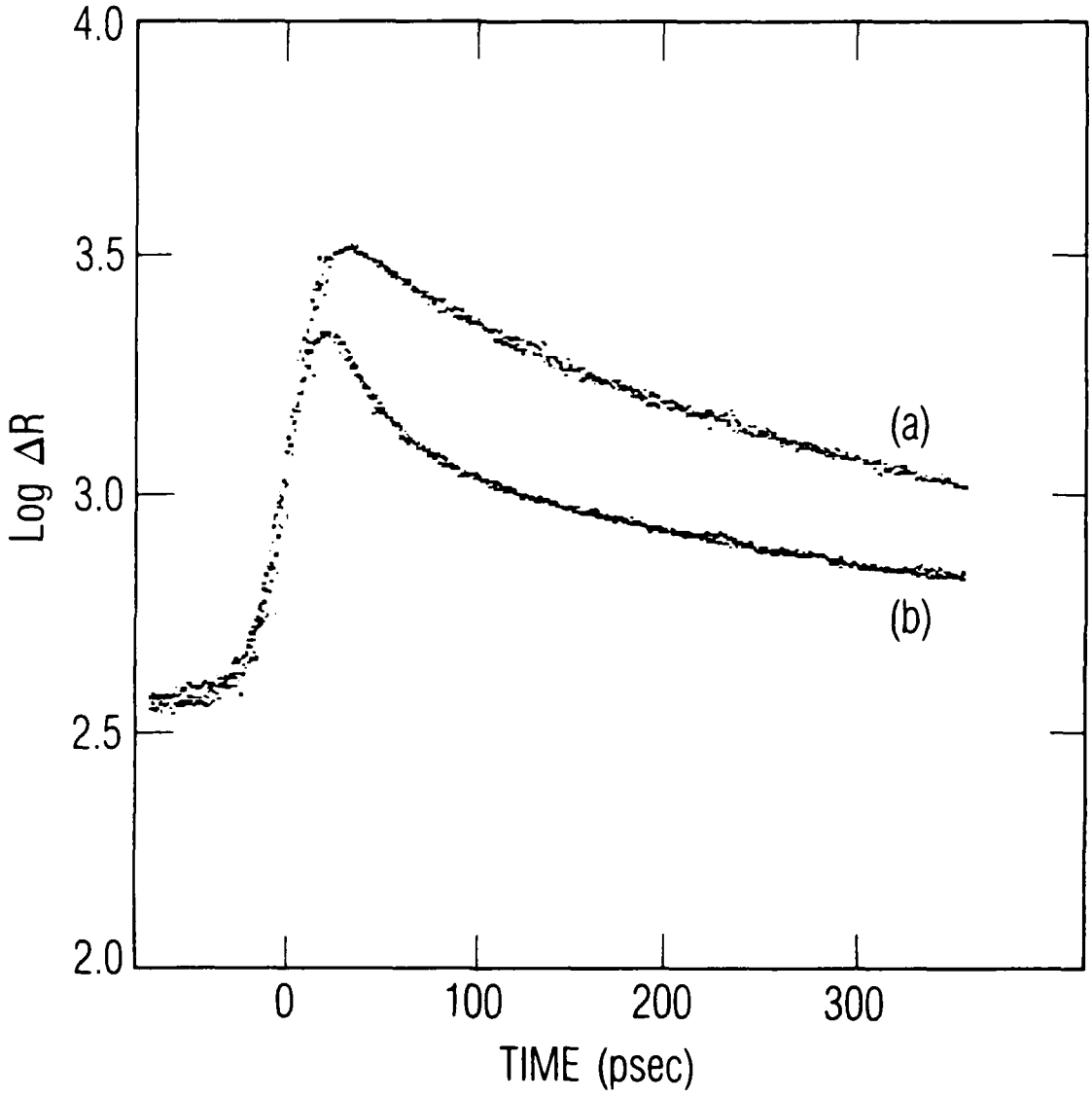

Fig. 1. Experimental Data for Silicon n-Doped GaAs Samples: (a) Photo-Washed, (b) Unwashed Surface. The vertical scale represents changes in reflectivity induced by the pump beam, and the horizontal scale is the time delay (arbitrarily scaled) between pump and probe beams.

IV. DISCUSSION

The preceding results for unwashed GaAs clearly represent measurement of fast surface processes. The fact that photochemical washing eliminates the fast, sample-dependent reflectivity decay of the unwashed samples proves that surface processes dominate reflectivity dynamics for the unwashed material. This is consistent with the proposal by the IBM group that arsenic and its oxides provide high densities of midgap surface states that promote recombination.

In an attempt to understand the relationship between surface recombination and reflectivity dynamics, we initiated numerical modeling studies of the recombination process. This work was based on extensive prior transient grating work on GaAs semiconductors, which involves dynamical modeling similar to that required for reflectivity studies. In particular, we use the equations derived by Hoffman et al.[4] for the carrier density as a function of surface recombination velocity (S), ambipolar diffusion coefficient (D), absorption coefficient (alfa), and bulk recombination time constant (TR). The relevant dynamics are described by Eq. (1) for DN, the change in carrier population, which included terms relevant to pure reflection experiments (and suppresses transient grating terms). Small reflectivity changes are assumed to be proportional to ΔN, evaluated at the surface.

$$\begin{aligned}\Delta N(Z,t) = N_o/2 \exp[-(t/TR)]\exp(-Z^2/4Dt)\{W[\alpha(Dt)^{1/2} - Z/2(Dt)^{1/2}] \\ + W[\alpha(Dt)^{1/2} + Z/2(Dt)^{1/2}] - [2(S/D)/(S/D-\alpha)] \\ \times\{W[\alpha(Dt)^{1/2} + Z/2(Dt)^{1/2}] - W[S/D(Dt)^{1/2} + Z/2(Dt)^{1/2}]\}\}\end{aligned} \quad (1)$$

with $W(X) = \exp(X^2)[1 - \mathrm{erf}(X)]$. (The treatment of penetration depth dependence of reflectivity by Aspnes and Frova[5] predicts that the reflection signal arises from a surface layer of depth 6×10^{-6} cm for our experimental conditions of $\alpha/2K \ll 1$, where K is the magnitude of the light momentum vector in the crystal.)

The calculation was first used to model results for photo-washed GaAs. Curves generated for several values of the surface recombination velocity are presented in Fig. 2. (The calculated curves were moderately insensitive to variation of the remaining parameters over the range of uncertainty.) Based on these curves, it is clear that the initial fast decay can only be obtained using a slow surface recombination velocity (2.3×10^5 cm/s), together with standard values for the ambipolar diffusion coefficient of 12 cm^2/s and a bulk recombination time of 8.5×10^{-10}s. Given these parameters, an exceptionally good fit is obtained for the reflectivity measurements, as shown in Fig. 1. This result supports the conclusion that a simple surface recombination model describes low intensity photo-induced carrier dynamics in GaAs prepared with relatively clean surfaces. The washing procedure appears to reduce surface recombination dramatically on all samples studied.

Kinetics of reflectivity for the unwashed samples are far more difficult to model. In Fig. 3, we show that the data cannot be described by the simple diffusion-surface recombination model. The initial fast decay implies a surface recombination velocity at least twice that for the washed samples. If the data are modeled by more complex expressions consisting of Eq. (1) plus an exponential term for the accurately exponential long component, then surface recombination velocities above 1×10^6 cm^2/s are required. These are closer to values previously suggested.[3,6]

A better model for the unwashed reflectivity kinetics would treat carrier transport in the presence of strong surface band bending. For n-doped material, the electrons would rapidly move away from the surface with a velocity determined by the product of the electron mobility and the surface field. This process would eliminate the band bending, and a regime of electron diffusion back to the surface would ensue. At present we do not know if this type of unified model would uniquely describe data for the unwashed surfaces. The fact that this treatment is not required to treat kinetics of the washed surfaces supports the suggestion by the IBM group that band bending is removed by the washing procedure. The ambipolar diffusion model should be valid for the resultant field free surface regions.

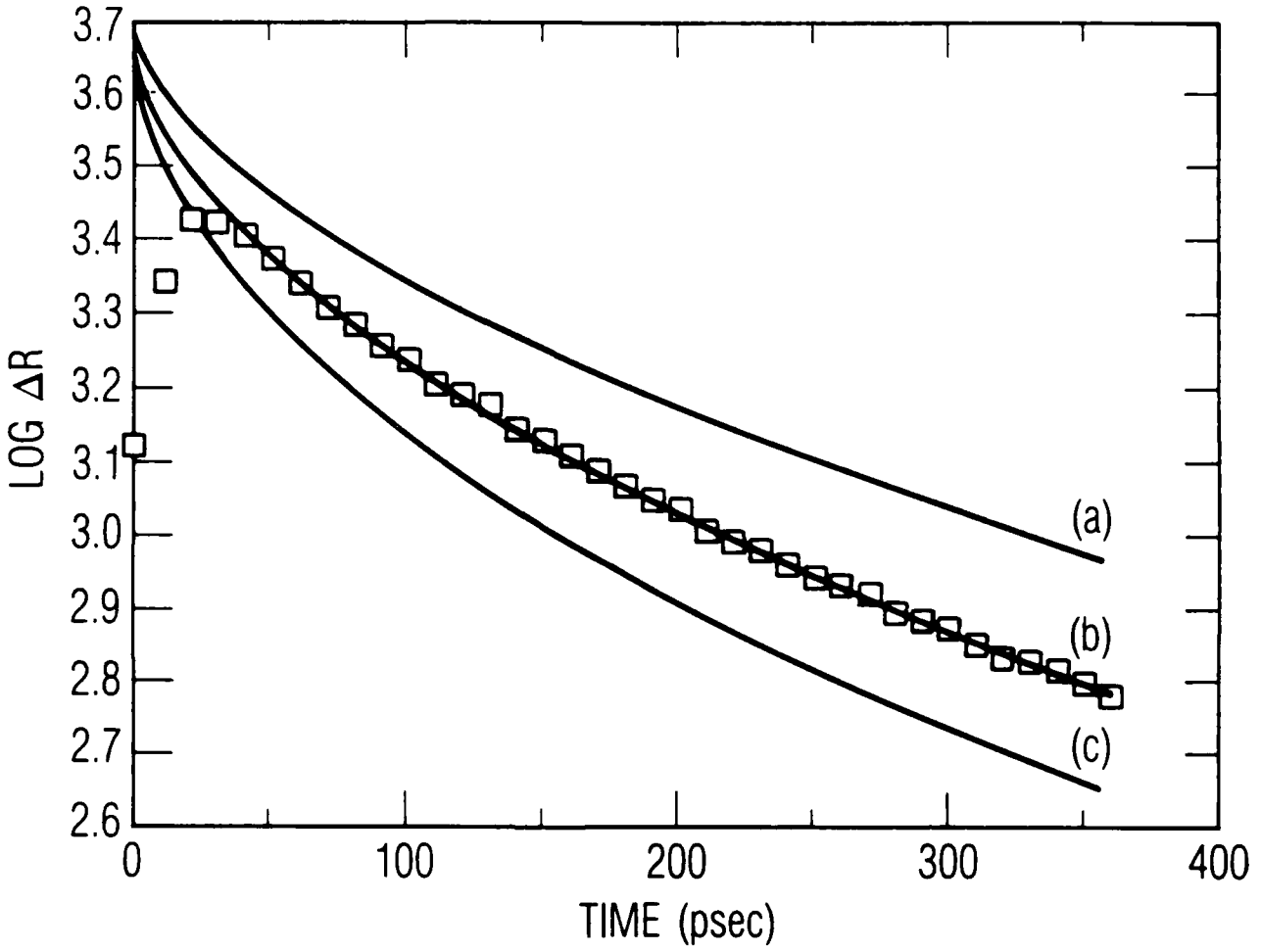

Fig. 2. Transient Reflectivity Decay Curves Calculated for Diffusion and Recombination at the Surface and in the Bulk Are Compared to Experimental Measurement on a Washed Sample (Designated X). Curves are presented for various surface recombination velocities: (a) 1.5×10^5 cm/s, (b) 2.0×10^5 cm/s, and (c) 2.5×10^5 cm/s, with values of 12 cm^2/s for the diffusion coefficient and 4×10^{-9}s for the bulk recombination time.

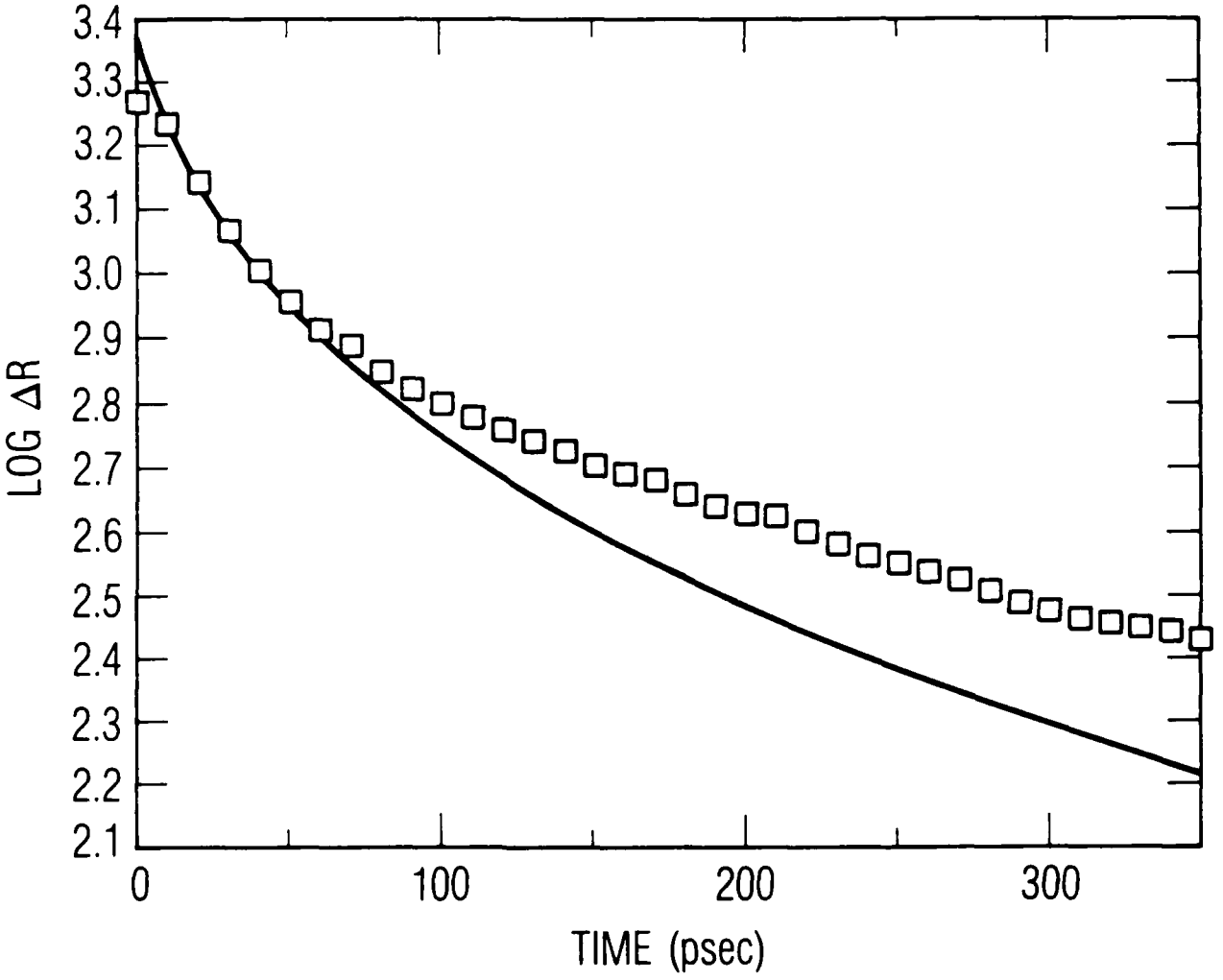

Fig. 3. Experimental Data (Designated X) for an Unwashed Silicon n-Doped GaAs Sample Are Compared to Transient Reflectivity Decay Curves Calculated, as in Fig. 2. Curves are presented for various surface recombination velocities: (a) 2.5×10^5 cm/s, (b) 5.0×10^5 cm/s, and (c) 1.0×10^6 cm/s, with values of 12 cm^2/s for the diffusion coefficient and 4×10^{-9} s for the bulk recombination time.

V. CONCLUSIONS

In conclusion, we demonstrated that surface recombination of GaAs can be quantitatively measured by picosecond transient reflectivity measurements. Furthermore, the results are extraordinarily sensitive to GaAs surface conditions, indicating that the surface dominates charge carrier transport at depths to 1 μm below typical unwashed surfaces. Clearly, the technique can provide a valuable quantitative measure of surface quality. One interesting and unresolved aspect of the work is that the rate of degradation of surfaces subsequent to photo-assisted washing seems to be different when measured by reflectivity as opposed to that deduced from photoluminescence. This, and the issue of the appropriate model for the fast recombination of unwashed surfaces, will be pursued in future studies.

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